

# Supercritical water oxidation of spent extraction solvent simulants\*

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(Received September 4, 2014; accepted in revised form March 5, 2015; published online June 20, 2015)

The rapid development of nuclear technology has led to more liquid organic radioactive wastes. Different from the regular aqueous radioactive wastes, these liquids possess a higher hazard potential and cannot be disposed through the conventional methods due to their radioactivity and chemical nature. Spent extraction solvent is a kind of common liquid organic radioactive wastes. In this work, tri-butyl phosphate (TBP), which is more difficult to degrade in the spent extraction solvent, was used as the model compound. Influences of reaction conditions on total organic carbon (TOC) removal and the volume percentage of each gas component under supercritical water oxidation (SCWO) were studied. The SCWO behaviors of spent extraction solvent simulants were studied under the optimal conditions derived from the TBP experiment. The SCWO experiments were studied at 400–550 °C, oxidant stoichiometric ratio of 0–200%, feed concentration of 1.5%–4% and pressure of 25 MPa for 15–75 s. The results show that the TOC removal of the simulants was greater than 99.7% and CH<sub>4</sub>, H<sub>2</sub> and CO were not detected at 550 °C, 25 MPa, oxidant stoichiometric ratio of 150%, feed concentration of 3%, and residence time of 30 s.

Keywords: Supercritical water oxidation, Liquid organic radioactive wastes, Spent extraction solvent, TBP

DOI: [10.13538/j.1001-8042/nst.26.030601](https://doi.org/10.13538/j.1001-8042/nst.26.030601)

## I. INTRODUCTION

Radioactive liquid wastes are generated from the use of radioisotopes in nuclear research centers or in medical and industrial applications [1, 2]. In recent decades, radioactive liquid wastes were increasing with the rapid development and application of nuclear techniques. They can be categorized into aqueous radioactive wastes and liquid organic radioactive wastes. Aqueous radioactive wastes can be well treated by radioactive wastewater treatment system. After the treatment phase, the wastes split into two portions. One is a small volume of concentrate that contain the bulk of radionuclides that is kept in the management system, while the other is a large volume portion of low radioactivity that allow its discharge to the environment when it meets the regulatory requirements [3]. By contrast, liquid organic radioactive wastes request management steps that take account of not only their radioactivity, but also their chemical contents. Because both radioactivity and organic chemicals have detrimental effects on health and environment, these wastes cannot be disposed through conventional methods due to their chemical nature [4, 5].

So far, incineration is an attractive treatment for disposal of liquid organic radioactive wastes, to destroy hazardous organics and reduce the mass significantly [6–8]. It is currently in use in a number of countries, such as Canada, France, the Russian Federation and the USA [7]. However, it is costly to build and operate an incineration facility. Also, it produces

toxic by-products in the offgas (e.g., furans and dioxins). Incineration requires additional fuel in treatment of wastes containing less than 30wt.% organic compounds, partially due to the high water content that need to be vaporized [9]. Problems of the incineration as also include agglomeration [10] and body corrosion [11]. So new technology needs to be developed for effective and safe disposal of the wastes.

Supercritical water oxidation (SCWO) is regarded as a promising technology for alternative to incineration due to its capability to treat hazardous industrial wastes and wastewaters, and has received enormous interests in the past decades [12–15]. Under supercritical conditions ( $P > 22.1$  MPa and  $T > 374$  °C), water possesses unique properties including negligible surface tension, high diffusivity, low viscosity, low inorganics solubility, and high organics solubility. Supercritical water shows complete miscibility with oxygen, creating a homogeneous reaction medium which makes it suitable for oxidation of liquid organics [16–18]. Generally, organics can be degraded completely in a few seconds without formation of toxic gaseous oxides (such as SO<sub>x</sub> and NO<sub>x</sub>) at 450–500 °C (while  $>1000$  °C for incineration).

Nowadays, many practical SCWO applications are seen in treatments of chlorinated hydrocarbons [19], municipal sewage sludge [20], etc. It is expected that liquid organic radioactive wastes can be decomposed efficiently in supercritical water, leaving radioactive nuclides in liquid effluent to be treated by radioactive wastewater treatment system. There are also some problems in SCWO, such as corrosion and plugging [21, 22] which can be solved in several ways, for example, selecting corrosion resistant reactor materials [23–25] and designing new type of reactors [26]. In our SCWO facility, the reactor and pre-heater are made of Inconel 625, a corrosion-resistant alloy under SCWO condition [27]. New type of reactor shall be designed and manufactured in our future works.

\* Supported by the “Strategic Priority Research Program” of the Chinese Academy of Sciences (No. XDA02050000)

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As one kind of liquid organic radioactive wastes, spent extraction solvent is generated from solvent extraction research, uranium refining, etc.. As the most commonly used extraction solvent, tri-butyl phosphate (TBP) is diluted for extraction process usually with light saturated hydrocarbon, such as *n*-dodecane or paraffin. Compared with aqueous radioactive wastes, spent extraction solvent contains organic matters of higher hazard potential due to their mobile, unstable and flammable characteristics. Therefore, effective management of these wastes should be carried out in order to ensure their safe handling, processing, storage and disposal.

In this paper, we take two steps to extend lifetime of the SCWO system and minimize the reactor corrosion, such as nitric acid corrosion. The first step is optimization of the reaction conditions of TBP which is difficult to degrade. TBP is treated under SCWO condition in a continuous-flow reactor, aimed at investigating effects of reaction conditions, such as oxidant stoichiometric ratio, residence time, feed concentration and temperature on the liquid and gas products. The second step is the SCWO experiments of the spent extraction solvent simulants.

## II. MATERIALS AND METHODS

### A. Apparatus and procedure

Figure 1 shows the SCWO-250 system, designed and fabricated by Supercritical Fluid Technologies, Inc (USA), consisting of one tank pre-heater (200 mL, Inconel 625) and one tank reactor (250 mL, Inconel 625). The facility can withstand up to 28.4 MPa and 600 °C. A back-pressure regulator provides precise control of system pressure. Under typical operating conditions, water and oxidant ( $\text{H}_2\text{O}_2$ ) flow rates range 1–100 mL/min, and feed flow rates range 0–36 mL/min. An on-line pH-probe with digital display is set before gas-liquid separator. The front panels allow access to the pressure vessel, valves, fittings, and electronics. Besides, as an additional safety precaution, two rupture disc assemblies provide mechanical protection against overpressure of the system. One is incorporated into the pipes between water pump and pre-heater, and the other is between cooler and back-pressure regulator.

At the beginning of each experiment, the temperature and pressure of both pre-heater and reactor were increased to the desired value with deionized water. Fluid composed of water and oxidant ( $\text{H}_2\text{O}_2$ ) was first introduced into the pre-heater by a high pressure metering pump (Pump 1). Then the feed solution was introduced into the reactor by another high pressure metering pump (Pump 2). The reactor was heated electrical coils around the reactor. The effluent, exiting from the top of the reactor, was cooled rapidly after passing through the cooler, and depressurized to ambient pressure through the back-pressure regulator. The temperature and pressure were controlled by a proportional integral derivative (PID) controller.

The effluent was introduced to the gas-liquid separator. The gas products were transported to gas chromatograph for composition analysis. The liquid products were sampled for

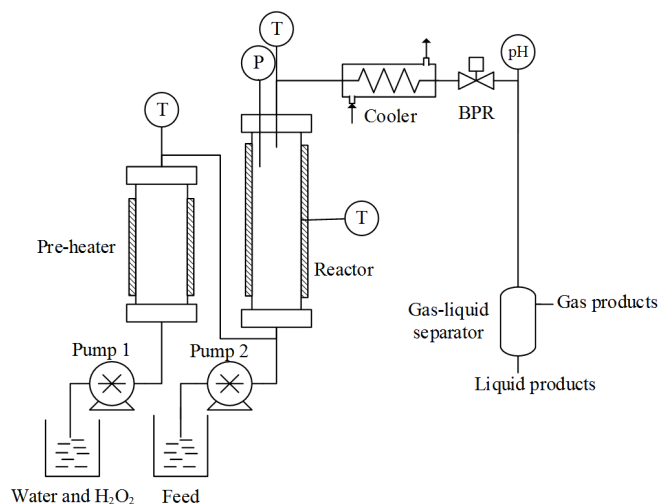


Fig. 1. Schematic diagram of SCWO system.

three times within 40 min after a 20-minute stable running, and the total organic carbon (TOC) in the liquid products was analyzed.

### B. Materials and analytical methods

Tri-butyl phosphate (TBP, purity of 98.5%), hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30%, w/w) and nitric acid ( $\text{HNO}_3$ , purity of 65%–68%) were purchased from Sinopharm Chemical Reagent Co., (China). *N*-dodecane (purity of 97%) and di-butyl phosphate (HDBP, purity of 97%) were purchased from Sigma-Aldrich Co. (Germany). Deionized water was prepared using a Milli-Q, ultrapure water purification system with a 0.22- $\mu\text{m}$  filter. Total organic carbon (TOC) in liquid products was analyzed with a TOC analyzer (Shimadzu TOC-L CSH, Japan). Measurement results of the three samples were averaged as the TOC removal. The gas composition was determined by a gas chromatograph (Agilent GC 7890A, Agilent Technologies, Inc. USA). It is equipped with thermal conductivity detector (TCD) and a G3591-80013 Q packed column, using helium as the carrier gas in flow rate of 40 mL/min; and with flame ionization detector (FID) and a G3591-80013 Q packed column, using  $\text{N}_2$  as the carrier gas in flow rate of 40 mL/min. The column, TCD detector and FID detector were kept at 50, 250 and 300 °C, respectively.

### C. Feedstock

*N*-dodecane is commonly used as diluent in TBP- $\text{HNO}_3$  extraction system. The TBP/diluent composition is 30 vol.% of TBP and 70 vol.% of *n*-dodecane, which is a classical mixing proportion in nuclear industry. The degradation products of TBP/diluent system is mainly HDBP caused by hydrolysis and radiolysis in fuel reprocessing process. HDBP is hydrolyzed in the presence of  $\text{HNO}_3$  and forms  $\text{H}_2\text{MBP}$ . The amount of  $\text{H}_2\text{MBP}$  formed is generally negligible [28].

TABLE 1. Composition and concentration of spent extraction solvent simulants

Composition	TBP	<i>n</i> -dodecane	HDBP	HNO <sub>3</sub>
Concentration (g/L)	284.2	507.7	0.276	47

Therefore, TBP, HDBP, *n*-dodecane and HNO<sub>3</sub> are the major components of spent extraction solvent. The concentration of HDBP and HNO<sub>3</sub> varies in different types of extraction experiments. A mid-value concentration of each component was used as the mixing recipe for spent extraction solvent simulants, i.e., HDBP of 276 mg/L and HNO<sub>3</sub> of 0.5 mol/L according to the literature [29], as given in Table 1.

#### D. Calculation

The residence time ( $t$ ) is related to feed rate ( $Q$ ), reaction temperature and pressure, as described in Eq. (1)

$$t = (V_0/Q)(V/V_r), \quad (1)$$

where  $V_0 = 250$  mL is the reactor volume;  $Q$  and  $V$  are the volumetric flow rate and specific volume of liquid effluent under room temperature and pressure conditions, respectively; and  $V_r$  is the specific volume of feedstock under reaction temperature and pressure.

The oxidant stoichiometric ratio can be calculated using Eq. (2):

$$\text{Oxidant stoichiometric ratio} = ([\text{H}_2\text{O}_2]_r/[\text{H}_2\text{O}_2]_0) \times 100\%, \quad (2)$$

where  $[\text{H}_2\text{O}_2]_0$  is the concentration theoretically required for complete oxidation of organic matters according to the stoichiometry of reaction, and  $[\text{H}_2\text{O}_2]_r$  is the specific concentration used in each experiment.

The *TOC removal* of liquid effluent was calculated using Eq. (3)

$$\text{TOC removal} = (1 - \text{TOC}_L/\text{TOC}_0) \times 100\%, \quad (3)$$

where,  $\text{TOC}_L$  is the concentration of total organic carbon in the liquid effluent; and  $\text{TOC}_0$  is the concentration of total organic carbon in the feedstock with the consideration of dilution effect of H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub>, which is obtained by theoretical calculations. The composition of gas products was determined by GC.

### III. RESULTS AND DISCUSSION

#### A. SCWO of TBP

All experiments for supercritical water oxidation were performed at about 25 MPa. In this part, effects of oxidant stoichiometric ratio, feed concentration, residence time and temperature on *TOC removal*, and composition of the gas products, were studied.

#### 1. Effects of oxidant stoichiometric ratio

The TBP was treated at 500 °C, 25 MPa, 3% feed concentration, 45 s residence time, and different oxidant stoichiometric ratios (0%–200%). The pre-heater was heated to 400 °C, and H<sub>2</sub>O<sub>2</sub> was completely converted to O<sub>2</sub> [30]. Fig. 2 shows that the *TOC removal* increases rapidly with oxidant stoichiometric ratio, from *TOC removal* of ~ 67% without oxidant. This indicates that water plays a key role in chemical reactions under the SCWO condition. Water acts as a reactant/product in bond-breaking reactions like hydrolysis, or as a supplier of hydrogen atoms under SCWO condition. Besides, it produces a high concentration of H<sup>+</sup> and OH<sup>-</sup> ions, which influence acid- or base-catalyzed reactions greatly [31]. The *TOC removal* was 85%, 98%, 99.2% and 99.5% at 50%, 100%, 150% and 200% of the oxidant stoichiometric ratio, respectively. Higher oxidant stoichiometric ratio increases the OH· and O<sub>2</sub> concentrations. OH· is a powerful oxidizing species [32], so degradation of the organics increases with oxidant stoichiometric ratio. From Fig. 2, oxidant stoichiometric ratio of 150% is sufficient for complete decomposing of TBP due to *TOC removal* of over 99%.

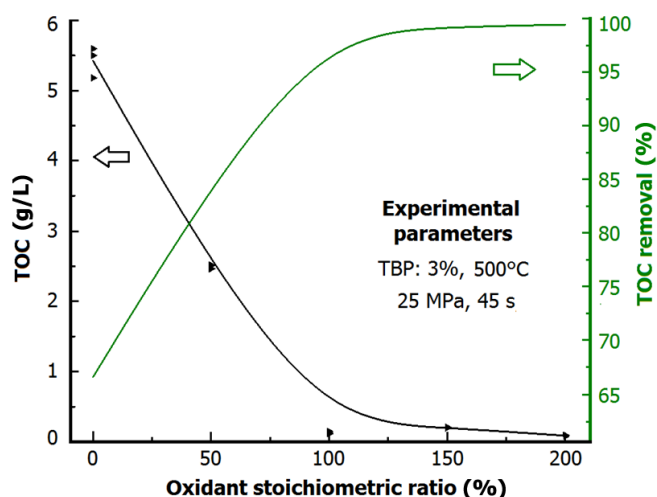
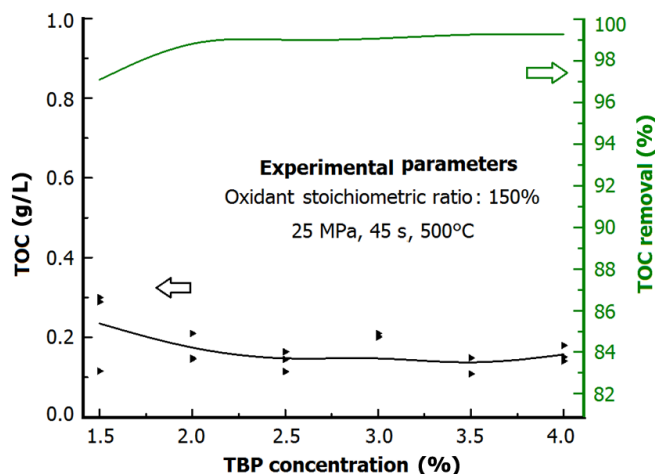
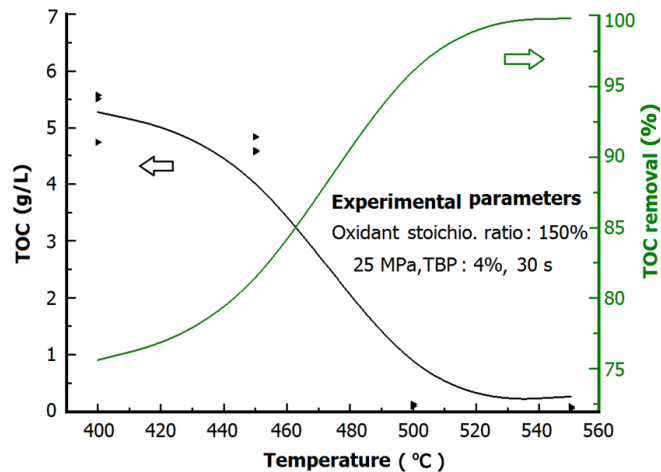


Fig. 2. (Color online) Effects of oxidant stoichiometric ratio on *TOC removal*.

#### 2. Effects of feed concentration

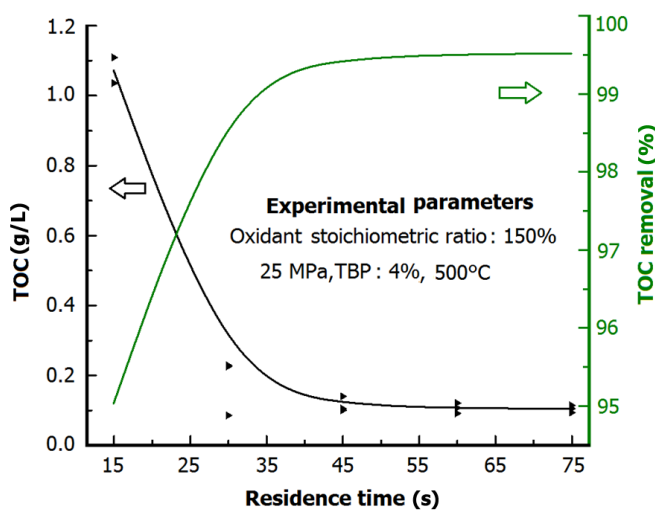
Effect of the TBP concentration on *TOC removal* at 500 °C, 25 MPa, and oxidant stoichiometric ratio of 150%, and residence time of 45 s is shown in Fig. 3. The initial feed concentration seems to have slight influences on the *TOC destruction efficiency*. At feed concentration of 1.5% and  $\geq 2\%$ , the *TOC removal* was about 97% and  $>99\%$ , respectively. SCWO showed a great processing capacity for organics. At higher feed concentration, more reaction heat is released, which leads local overheating, hence the increased degradation of the organics. The maximum TBP concentration applied in this work was 4wt.%, being greater than those in lit-

Fig. 3. (Color online) Effects of TBP concentration on *TOC removal*.Fig. 5. (Color online) Effects of temperature on *TOC removal*.

eratures [33, 34], due to the restriction of oxidant concentration.

### 3. Effects of residence time

Organics can be degraded rapidly under SCWO condition [35]. Figure 4 shows the residence time effect on *TOC removal* at 500 °C, 25 MPa, feed concentration of 4% and oxidant stoichiometric ratio of 150%. An increase in the residence time showed a positive influence on *TOC removal* of liquid products. At residence time of 15 s and 30 s, the *TOC removal* was about 95% and >99%, respectively. The residence time effect became less important as it exceeded a threshold. In this work, residence time of about 30 s was considered to be effective and affordable.

Fig. 4. (Color online) Effects of residence time on *TOC removal*.

### 4. Effects of reaction temperature

In the SCWO process of organics, temperature is an important factor. Figure 5 shows the temperature effect on *TOC removal* at 25 MPa, 4% feed concentration, 150% oxidant stoichiometric ratio and 30 s residence time. The *TOC removal* of liquid products increases rapidly with the temperature. At 550 °C, the *TOC removal* reaches a maximum of about 99.7%. Temperature affects degradation of organics in three ways. Firstly, the reaction rate constant  $k$  increases exponentially with temperature, hence the acceleration of the reaction process [36, 37]. Next, the reaction medium density decreases with increasing temperature, which means the decreased concentration of reactants, hence the reduced reaction rate. Finally, the residence time decreases with increasing temperature.

### 5. Effects of oxidant stoichiometric ratio and temperature on gas products

The experiments were carried out at different reaction temperatures (400, 450, 500 and 550 °C) in different oxidant stoichiometric ratios (50%, 100% and 150%), at 25 MPa, residence time of 30 s, and feed concentration of 4%. Fig. 6 illustrates the volume proportion of  $\text{CH}_4$ ,  $\text{H}_2$ ,  $\text{CO}$  and  $\text{CO}_2$ , excluding  $\text{O}_2$  and other gases in small volume, as a function of oxidant stoichiometric ratio. As expected, the oxidant stoichiometric ratio has a significant impact on the yield of the gases. The yields of  $\text{CH}_4$ ,  $\text{H}_2$  and  $\text{CO}$  decrease gradually with increasing oxidant stoichiometric ratio, being undetectable at oxidant stoichiometric ratio of 150%; whereas the  $\text{CO}_2$  yield increases steadily with oxidant stoichiometric ratio. The maximum volume percentage of  $\text{CH}_4$ ,  $\text{H}_2$  and  $\text{CO}$  was 9.4% at 400 °C, 6.07% at 400 °C and 45.11% at 450 °C, respectively, at oxidant stoichiometric ratio of 50%. The maximum volume percentage of  $\text{CO}_2$  was 99.99% at 550 °C and oxidant stoichiometric ratio of 150%. In addition, for oxidant stoichiometric ratio of 50%, temperature affects significantly the

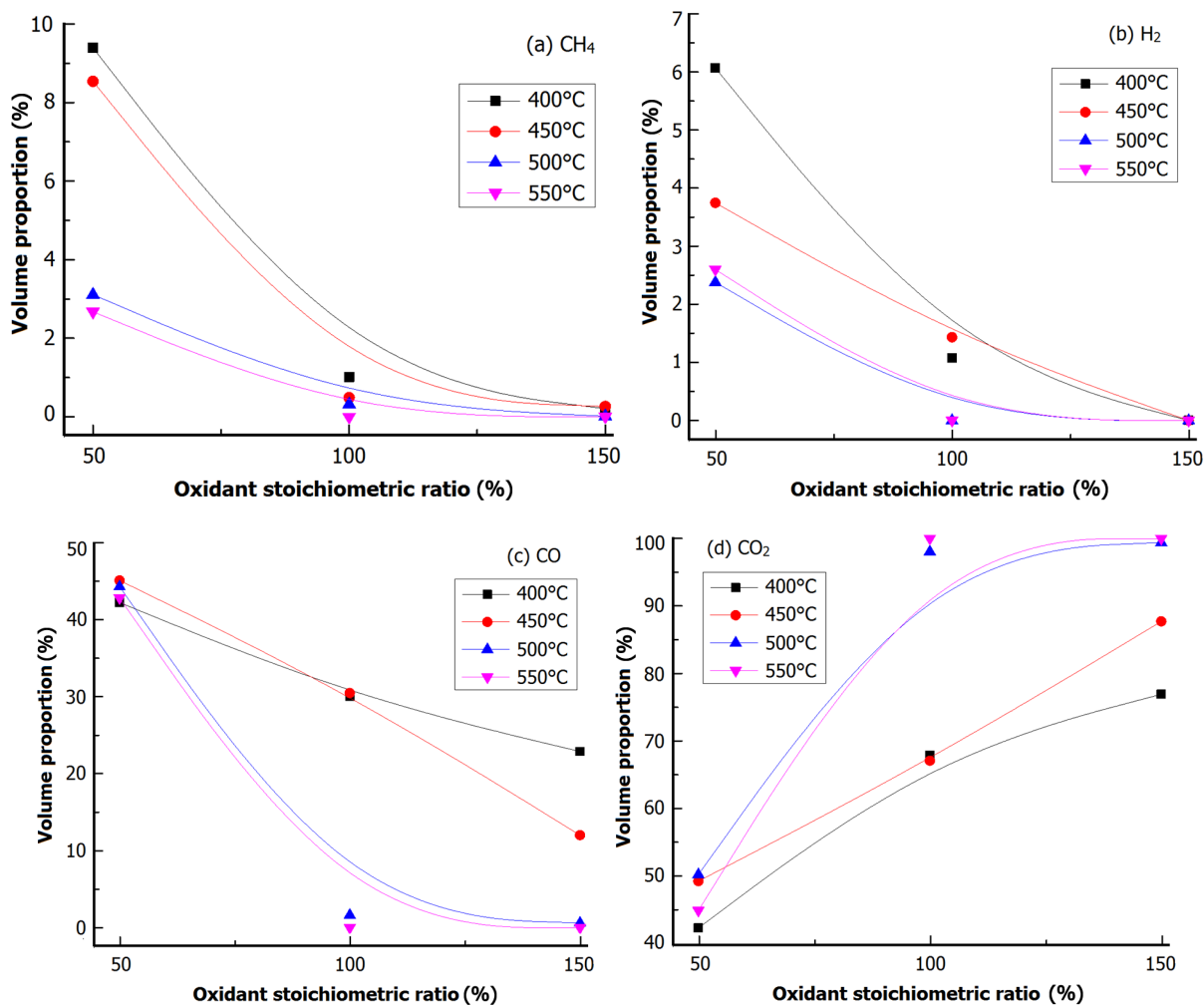


Fig. 6. (Color online) Effects of oxidant stoichiometric ratio and temperature on the yield of CH<sub>4</sub>, H<sub>2</sub>, CO and CO<sub>2</sub>.

yields of CH<sub>4</sub> and H<sub>2</sub>, which decrease with increasing temperature. Temperature has little effect on the yields of CO and CO<sub>2</sub> for oxidant stoichiometric ratio of 50%, but at higher oxidant stoichiometric ratios the temperature effect becomes obvious. This is because that partial oxidation occurs at lower temperature and oxidant levels, which produced the intermediates and hydrogen. At higher temperatures or oxidant levels, the intermediates and hydrogen may be further oxidized to end products, such as carbon dioxide and water.

### B. SCWO of spent extraction solvent simulants

The TOC removal of the simulants under the optimal conditions (550 °C, 25 MPa, 3% feed concentration, 150% oxidant stoichiometric ratio and residence time of 30 s, derived from the above experiments) were (99.77 ± 0.02)%, with the TOC measured in three samplings being 35.32, 39.96 and 36.75 ppm.

We also investigated the effects of oxidant stoichiometric ratio on the volume percentage of each gas component at

TABLE 2. Influences of different oxidant stoichiometric ratios on volume percentage of each gas component under optimal conditions

Oxidant stoichiometric ratio(%)	CH <sub>4</sub> (v/v %)	H <sub>2</sub> (v/v %)	CO (v/v %)	CO <sub>2</sub> (v/v %)
50	7.14	3.7	29.97	59.18
100	0.04	0.79	0.31	98.86
150	— <sup>a</sup>	— <sup>a</sup>	— <sup>a</sup>	99.99

<sup>a</sup> Not detected

550 °C, 25 MPa, 3% feed concentration, and residence time of 30 s. Table 2 shows the volume percentage of CH<sub>4</sub>, H<sub>2</sub>, CO and CO<sub>2</sub> for different oxidant stoichiometric ratios. The volume percentage of CH<sub>4</sub>, H<sub>2</sub> and CO gradually decreased with increasing oxidant stoichiometric ratio, but CH<sub>4</sub>, H<sub>2</sub> and CO were undetectable at 150% of oxidant stoichiometric ratio, while the volume percentage of CO<sub>2</sub> increased steadily with the ratio. It shows the same behavior with that of TBP as described in Section III A 5.

## IV. CONCLUSION

The SCWO behavior of TBP and spent extraction solvent simulants was studied in this work. And we investigated the influence of different reaction factors on *TOC removal* and gas products. We came to the conclusion that the optimal conditions for treatment of spent extraction solvent simulants by the comprehensive analysis of different factors, that is, reaction temperature of 550 °C, pressure of 25 MPa, oxidant stoichiometric ratio of 150%, feed concentration of 3%,

and residence time of 30 s. The *TOC removal* of spent extraction solvent simulants was greater than 99.7%, and no CH<sub>4</sub>, H<sub>2</sub> and CO were detected under optimal conditions. Oxidant and temperature played important roles in the yield of CH<sub>4</sub>, H<sub>2</sub> and CO during the decomposition of spent extraction solvent simulants. The residence time presented a significant impact until it exceeded a threshold, which is 30 s in this research. The initial feed concentration had slight influences on the *TOC removal*. This work will lay the foundation for the SCWO investigation of radioactive wastes.

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